

Interactive comment on “Aluminium and base cation chemistry in dynamic acidification models – need for a reappraisal?” by Jon Petter Gustafsson et al.

Jon Petter Gustafsson et al.

gustafjp@kth.se

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First we would like to thank the reviewer for very good comments, which helped us to improve the quality of the manuscript. Below we provide a point-by-point response to the details brought up by the reviewer. To start with, we list all comments where we agree completely with the reviewer, and where we have simply followed the recommendations without any comments or reservations:

Page 1, line 15: $H^+ \rightarrow H^+$ Page 1, line 15: Delete ‘Consequently, ‘: The sentence is not a real consequence of the previous one (it’s always true). Page 1, line 18: Insert ‘model’ after ‘HD-MINTEQ’ Page 3, line 1: Insert ‘model as a basis’ (or ‘as a basis’)

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after ‘SHM’. Page 4, line 18: It could/should be mentioned that in SMART/VSD the user can choose between a Gapon or Gaines-Thomas exchange model. Page 5, line 31: Insert ‘the’ before ‘UK’. Page 5, line 32: Why ‘however’ after ‘In one paper’? Suggest deleting! Page 11, line 29: ‘longest’ \rightarrow ‘longer’. Table 1: Caption: Maybe expand text? Write ‘humic acids’ and ‘fulvic acids’ instead of ‘HA’ and ‘FA’, resp., in the first column. Table 2: Add ‘scenario’ after ‘Background-acid-background’ and after ‘Background-salt’ in the first line if the Table. Figure 1, 2 and 3: Caption: (a) Insert ‘in the four soil layers (O, E, B1, B2)’ before ‘as a function’; (b) insert ‘deposition’ before ‘scenario’. Figure 5: For ‘aesthetic reasons’ maybe interchange in the legends the lines ‘SHM’ and ‘Ion exchange B’ (twice) (?)

Below we provide a more detailed response to the other comments:

Page 6, line 1: What does the stand-alone ‘Ki’ in eq.6 mean? In the next line it is referred to as ‘Here the Ki is ...’? ANSWER: This is a common way to clarify that there is an equilibrium constant that defines the relationship between the products and the reactants, but it is not an important clarification. However, since this is not really needed, we have decided to remove the K. The sentence that follows has been changed as a consequence.

Page 6, line 30: Eq.8 does not make sense: If I insert $i=1,2,3,4$ into it, I get 4 times the identical value for $\log K_1, \dots, \log K_4$, since the right-hand side of eq.8 does not depend on the index i !! Correct! ANSWER: Thank you for pointing this out. Something had happened with an equation object that we had inserted, and therefore a term was missing. This has now been fixed.

Page 6, line 31: Same again!!

ANSWER: See above comment.

Page 8, line 2: There is no Q_i in equations (10) or (11), thus one cannot solve for them!! ANSWER: There is no error here - these equations should be seen as part

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of an equation system that is solved simultaneously. We have included the following sentence for clarification: “To calculate the partitioning of the reacting ions, Eqs. (10-12) are solved simultaneously as described by Kinniburgh et al. (1999).”

Page 11, line 6: It is not essential, but the scenario name is a bit ‘strange’; and, actually slightly misleading, since the 3rd interval is not background depo (but close). ANSWER: Valid point, we agree and have changed the scenario names as suggested by the reviewer

Page 11, line 8: Also this name is not ‘unconfusing’ . . . Why not just call the ‘Acid’ and ‘Salt’? – just a thought . . . ANSWER: See previous comment

Page 11, line 13: Should it be ‘(Gustafsson, 2016)’, as in the References; or is the year there wrong? ANSWER: The year given in the reference was wrong, it has now been changed to 2018

Page 12, line 2: Also in SMART/VSD H+ exchange is modelled! ANSWER: Correct, SMART/VSD has been added

Page 13, line 5: ‘(Gustafsson, 2016)’? ANSWER: No, as written above the year is 2018

Page 13, line 29: ‘SMART/VSD’ could be added (?) ANSWER: OK, it has been added. Similarly, we have also added SMART/VSD in the Abstract in two instances.

Page 14, line 12: The ending is a bit abrupt . . . ANSWER: You are right, a Conclusions section is missing. We have now added a Conclusions section to the paper. It reads as follows:

“Ion-exchange equations, despite being relatively simplistic, predict the same type of response to changes in input chemistry as more advanced organic complexation models such as SHM, NICA-Donnan and WHAM. This is particularly true in cases when the pH variations with time are relatively small. If larger pH variations occur the differences in predicted pH and cation binding will be larger. The main reason for this is the acid-base chemistry of organic matter, for which acid dissociation occurs over a wide

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pH range. This effect is not captured correctly by the ion-exchange equations. For example, this may be an important point to consider for model initialization, as the soil water pH may have been much higher under preindustrial conditions than it was later during the acid rain era. The value of exchangeable Ca²⁺ was found to be particularly sensitive in this regard. The method used to account for Al chemistry, i.e. whether or not letting the solubility of Al³⁺ to be determined by a fixed gibbsite constant, was less important. Although a fixed gibbsite constant did cause stronger pH buffering than a more advanced model combining organic complexation and Al(OH)₃ precipitation, the effect was rather small. In summary, state-of-the-art organic complexation models should be preferred over ion-exchange equations for predicting pH and cation binding in dynamic acidification models, particularly if large pH variations occur during the simulated time period.”

Page 15, line 24: Is it Gustafsson 2016 or 2018? ANSWER: Gustafsson, 2018, as explained above

Figure 1, 2 and 3: The dotted red line is not visible in the graphs as such! Why not use solid lines with 4 (sufficiently) different colours? ANSWER: Parts of the dotted lines do not appear as dotted (rather as solid) because of the very large number of points and because of the fact that there are frequent very small spikes in the simulation lines, we regret that. On the other hand, our reason for plotting some of the lines in rather similar colours is that it is then easy to quickly distinguish between the ion-exchange models (red-orange) and the organic complexation models (blue-green). Hence there is a slight conflict between the desire to quickly identify the exact data set and the desire to quickly distinguish the two groups of data. We have, for now, decided to keep the lines and colours unchanged.

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